

## METHANOL SYNTHESIS STUDIES USING IN SITU FTIR SPECTROSCOPY

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Annual methanol demand in this country has been projected to double during the 1980s to 8 million metric tons due mainly to rapid expansion in several developing applications (1). Major uses for methanol are the production of formaldehyde, dimethyl terephthalate (DMT), methyl methacrylate, methyl halides, methyl amines, and acetic acid. Large quantities of methanol are used as a gasoline blending agent and as a solvent. Legislated reductions in the amount of tetraethyl lead allowed in gasoline have increased the demand for octane boosters such as methyl tert-butyl ether (MTBE) which is made from methanol and isobutylene. The recent development of a single-step catalytic distillation process (MTBE plus) which eliminates the methanol recovery section of the conventional process, provides an economically attractive alternative to isobutylene alkylation for octane enhancement (2). Methanol by itself can be used as an octane booster, but there are problems with methanol/gasoline mixtures due to their higher affinity for water, higher evaporative losses, and the need to modify the engine.

Future demand for methanol could expand multifold as coal assumes a greater proportion of our energy needs. Although methanol is presently economically unattractive as a substitute for gasoline, the State of California has begun a program to operate 550 vehicles with methanol because it produces fewer pollutants than gasoline. More than 300 privately-owned vehicles, converted by Future Fuels of America, Inc., are running on methanol in the Sacramento, San Francisco, and Los Angeles areas. Even if gasoline remains the major automotive fuel into the next century, methanol production could increase significantly if technology such as Mobil Oil's M-Gasoline process is used to produce gasoline. This process uses a zeolite catalyst (ZSM-5) to convert methanol into a blend of paraffins, cycloparaffins, and aromatics with a research octane number of 93, i.e., an unleaded premium gasoline (3). New Zealand will use this technology to convert natural gas into approximately 12,500 bbl/d of gasoline. Utilities using coal gasification technology for power generation will probably also manufacture methanol. During off-peak hours, part of the syngas would be converted to methanol and stored; during peak hours, the methanol would be used as fuel in gas turbines to meet the high electrical demand. And finally, there is great potential for future development of methanol as a primary feedstock in the chemical industry, especially as supplies of ethylene and propylene decrease. An example is the manufacture of acetic acid, where methanol has replaced ethylene as the primary feedstock in new technologies by BASF and Monsanto (4).

The key development in methanol synthesis technology has been the catalyst. Improvements in catalyst performance are usually obtained by trial-and-error methods: variations in composition or preparation technique are tried until a catalyst is found having greater activity, selectivity, or stability. Characterization of physical and chemical properties is often incomplete, and the reasons for the superiority of a particular catalyst are frequently unclear. Although methanol synthesis as a commercial process is fully developed, the specific function of the catalyst and the fundamentals of the elementary surface reactions are still highly speculative. The main objective of this investigation has been to prepare several different compositions of methanol synthesis catalysts and characterize these catalysts by physical and chemical techniques, placing emphasis on the use of Fourier transform infrared (FT-IR) spectroscopy to identify the chemical species adsorbed on the catalyst surfaces under methanol synthesis conditions. It should be emphasized that this study has focused on the FT-IR characterization of adsorbed surface species under in situ conditions with the objective of obtaining a better understanding of the molecular interactions occurring on the catalyst surface.

In spite of advances in the characterization of methanol catalysts, the nature of adsorbed species and of the elementary surface reactions continues to be uncertain. Several mechanisms for methanol synthesis have been proposed in recent years. A chemical trapping technique has identified formate and methoxy species on a used methanol catalyst (5); the proposed methanol synthesis mechanism postulates that formate, methyloxy, and methoxy groups are reaction intermediates bonded through oxygen to a metal ion site. A much different mechanistic proposal was suggested by Herman and co-workers (6) involving carbonyl, formyl, hydroxycarbene, and hydroxymethyl intermediates bonded through carbon to a Cu(I) ion in the zinc oxide phase. Adjacent zinc ions were the centers for hydrogen adsorption. A recent revision of this mechanism has incorporated hydroxyl, formate, formyl, and methoxy species bonded to a Cu(I) ion in the reaction pathway (7). Other mechanisms have been proposed incorporating both carbon-bonded and oxygen-bonded intermediates in methanol synthesis. A reaction scheme with carbonyl, formyl, formaldehyde, and methoxy intermediates adsorbed on Cu(I) active sites within the zinc oxide lattice was developed from a review of the literature (8). This mechanism was analogous to methanol synthesis by homogeneous catalysis. Another mechanism has proposed that an oxygen vacancy acts as an active site in methanol synthesis (9). After a carbonyl species is hydrogenated to a formyl species, the oxygen on the formyl interacts with an adjacent electron-deficient vacancy. As further hydrogenation occurs, a methoxy species is formed as the bonding between the oxygen and vacancy is strengthened while the bonding between the carbon and metal ion weakens. The variation in catalytic activity with specific crystal planes of zinc oxide has been ascribed to the relative number of defects (vacancies) in each type of plane (10,11).

The catalysts were prepared by coprecipitating a mixture of metal nitrates with ammonium bicarbonate at 60°C according to the method described by Stiles (12). After filtering and washing with distilled water, the precipitates were dried in air at 115°C for 12 h and then calcined in a stream of oxygen at 400°C for 8 h. The amount of cupric oxide in these catalysts was restricted to no greater than 10% CuO due to the strong infrared absorption by cupric oxide.

The oxidic form of the catalyst was prepared for transmission infrared studies by pressing powder under a load of 4500 kg into a wafer approximately 0.10 mm thick and placing the wafer into the infrared cell. Catalyst activity and selectivity evaluations were conducted in a fixed-bed tubular reactor containing a bed of broken catalyst wafers surrounded by SiC particles. Dry nitrogen gas was flowed through the infrared cell or reactor for approximately 12 h at atmospheric pressure and 200°C to desorb water on the catalyst surface. Under these conditions there was no significant dehydroxylation of the catalyst surface. All experiments were conducted in a continuous flow mode at 60 cm<sup>3</sup>/min (STP) using high-purity gases. Water or formic acid solution could be introduced into the feed system at low concentrations by bubbling the gaseous flow through the liquid which was contained within an enclosed stainless-steel vessel (saturator). Catalysts were reduced by exposing the oxide to a 95/5 N<sub>2</sub>/H<sub>2</sub> stream for 1 h at 200°C and 1 atm (pretreatment 1).

Binary catalysts with low copper contents (Cu/Zn ≤ 0.15) were satisfactory for transmission infrared studies in both oxidized and reduced states. During high-pressure *in situ* studies these catalysts had a significant transmittance loss at lower wavenumbers, requiring that the identification of adsorbed species be based on infrared bands above 2000 cm<sup>-1</sup>.

The adsorption of carbon monoxide on a 95/5 Zn/Cu catalyst at 200°C and 50 atm is shown in Fig. 1. The initial oxidized surface (Fig. 1a) had residual hydroxyls (bands at 3663, 3620, 3560, and 3455 cm<sup>-1</sup>) and carbonates (bands at 1515, 1469, 1376, and 1323 cm<sup>-1</sup>). Prolonged exposure to CO reduced the catalyst (Fig. 1b), indicated by the formation of the hydroxyl band at 3250 cm<sup>-1</sup>. Formate groups (bands at 2969, 2878, 2731, and 1573 cm<sup>-1</sup>), a zinc hydroxyl (band at 3520 cm<sup>-1</sup>), and a zinc hydride (band at 1660 cm<sup>-1</sup>) gradually developed. After 24 h (Fig. 1c) an adsorbed formaldehyde species (bands at 2935, 2834, and 2731 cm<sup>-1</sup>) had formed and the

carbonyl band had shifted to  $1975\text{ cm}^{-1}$ . (The band of gaseous CO at  $2143\text{ cm}^{-1}$  masked the carbonyl band in the earlier spectra.)

The hydrogenation of surface species was accelerated by incorporating hydrogen into the carbon monoxide feed. Figure 2 shows the adsorption of a mixture of carbon monoxide and hydrogen ( $\text{CO}/\text{H}_2 = 9/1$ ) on a 95/5 Zn/Cu catalyst at  $200^\circ\text{C}$  and 50 atm. Formate groups (band at  $2879\text{ cm}^{-1}$ ) and hydroxyls associated with reduction (band at  $3252\text{ cm}^{-1}$ ) were quickly formed (Fig. 2). The development of methoxy groups (bands at  $2934$  and  $2822\text{ cm}^{-1}$ ) (Fig. 2c) was accompanied by the disappearance of the isolated hydroxyls (bands at  $3660$  and  $3612\text{ cm}^{-1}$ ). The formate band shifted significantly from  $2879$  to  $2868\text{ cm}^{-1}$ , due to the development of the methoxy groups.

The adsorption of a stoichiometric  $2/1\text{ H}_2/\text{CO}$  mixture on 95/5, 90/10, and 85/15 Zn/Cu catalysts at  $200^\circ\text{C}$  and 50 atm after an hour of exposure is shown in Fig. 3. Very little detail could be observed at lower wavenumbers because of low transmittance. This surface condition would be representative of the adsorbed species during methanol synthesis. The spectra showed the hydroxyl of reduction (band at  $3252\text{ cm}^{-1}$ ), methoxy groups (bands at  $2933$  and  $2822\text{ cm}^{-1}$ ), and formate groups (bands at  $2865$  and  $1575\text{ cm}^{-1}$ ) in addition to the band for gaseous carbon monoxide at  $2143\text{ cm}^{-1}$ . The spectra of the 85/15 Zn/Cu catalyst was noisier than the other spectra because its transmittance was an order of magnitude lower than the others.

Methanol synthesis from a stoichiometric feed of carbon monoxide and hydrogen was compared with other feed mixtures. Figure 4 shows the nature of surface species on a 95/5 Zn/Cu catalyst at  $200^\circ\text{C}$  and 50 atm for various feed compositions that were previously established from reactor studies to be satisfactory for methanol synthesis. A feed mixture of  $66/27/7\text{ H}_2/\text{CO}/\text{CO}_2$  produced surface species that were identical with those using only  $\text{H}_2$  and CO in the feed. The additional band at  $2350\text{ cm}^{-1}$  was absorption by gaseous carbon dioxide. A feed mixture of  $50/50\text{ H}_2/\text{N}_2$  containing some formic acid solution ( $73\%\text{ HCOOH}$ ,  $27\%\text{ H}_2\text{O}$ ) also produced formate (band at  $2870\text{ cm}^{-1}$ ) and methoxy groups (bands at  $2935$  and  $2820\text{ cm}^{-1}$ ). Because the feed had some water and a low formic acid concentration, the isolated hydroxyls (bands at  $3660$  and  $3620\text{ cm}^{-1}$ ) were not completely displaced by methoxy groups.

The ternary Zn-Cu-Cr oxide catalysts, which were also restricted to low copper contents, were superior to the binary catalysts in high-pressure infrared experiments because the transmittance remained high throughout the mid-infrared range. Better surface detail provided more information for identifying adsorbed species during methanol synthesis conditions.

The reaction of carbon monoxide and hydrogen on a 90/5/5 Zn/Cu/Cr catalyst at  $200^\circ\text{C}$  and 50 atm is shown in Fig. 5. The initial surface species on the reduced catalyst (pretreatment 1) after exposure to a  $2/1\text{ H}_2/\text{CO}$  mixture (Fig. 5) were formate groups (bands at  $2963$ ,  $2872$ ,  $1582$ ,  $1381$ , and  $1360\text{ cm}^{-1}$ ), adsorbed formaldehyde species (bands at  $2934$  and  $2843\text{ cm}^{-1}$ ), and methoxy groups (bands at  $2934$  and  $2824\text{ cm}^{-1}$ ). The adsorbed formaldehyde species disappeared and the amount of methoxy groups reached a maximum in an hour (Fig. 5b), followed by a gradual decrease in methoxy groups (Fig. 5c). A pressure drop to 1 atm (Fig. 5d) revealed an adsorbed carbonyl species at  $2010\text{ cm}^{-1}$ .

The reaction of carbon monoxide and hydrogen ( $\text{H}_2/\text{CO} = 2/1$ ) on a 80/10/10 Zn/Cu/Cr catalyst (pretreatment 1) at  $200^\circ\text{C}$  and 50 atm is shown in Fig. 6. The initial spectrum (Fig. 6a) showed formate groups (bands at  $2870$ ,  $1576$ ,  $1381$ , and  $1360\text{ cm}^{-1}$ ), methoxy groups (bands at  $2932$  and  $2822\text{ cm}^{-1}$ ), and a carbonyl species at  $2089\text{ cm}^{-1}$ . The methoxy groups reached a steady-state condition within an hour (Fig. 6b). The carbonyl species shifted from  $2089$  to  $2021\text{ cm}^{-1}$  (Fig. 6c). A pressure drop to 1 atm (Fig. 6d) revealed in sharper detail a carbonyl species at  $2010\text{ cm}^{-1}$ .

Reactor tests established that although a binary catalyst was active for formic acid hydrogenation to methanol, the 80/10/10 Zn/Cu/Cr catalyst was inactive for this

reaction during the same operating conditions. The adsorption of formic acid solution (73% HCOOH, 27% H<sub>2</sub>O) in a carrier gas of 50/50 H<sub>2</sub>/N<sub>2</sub> on a 80/10/10 Zn/Cu/Cr catalyst (pretreatment 1) at 200°C and 50 atm is shown in Fig. 7. A carbonyl species (band at 1983 cm<sup>-1</sup>) and minor amounts of formate groups (bands at 2872, 1580, 1381, and 1360 cm<sup>-1</sup>) were the only adsorbed species formed within the first hour of exposure (Fig. 7b). Some methoxy groups (bands at 2934 and 2818 cm<sup>-1</sup>) were produced after prolonged exposure (Fig. 7c), but the concentration was low since the isolated hydroxyls (bands at 3668 and 3618 cm<sup>-1</sup>) were not completely displaced. Thus the poor methanol synthesis activity of Zn-Cu-Cr catalysts when using formic acid in the feed mixture was due to the difficulty of formic acid decomposition into formate groups and adsorbed hydrogen at high pressures.

Information about the sequence of reaction steps and adsorption sites was obtained from transient experiments. Despite the low activity of these catalysts at 200°C, the infrared spectra showed that steady-state surface conditions were quickly reached when a 2/1 H<sub>2</sub>/CO feed mixture was used. The surface reactions could be slowed by decreasing the amount of hydrogen in the feed mixture. Even in the extreme case of having only carbon monoxide in the gas phase, gradual hydrogenation of surface species occurred because the residual hydroxyls were a source of hydrogen. This demonstrated that hydrogen (possibly as protons) was mobile on the surface at 200°C. Formate groups were clearly formed before formaldehyde and methoxy groups. The order of formaldehyde and methoxy formation at high pressure was difficult to establish because the intensity of the formaldehyde bands was low, but results from the atmospheric studies (13) suggested that the formaldehyde species was the precursor of the methoxy species.

The spectra of Zn/Cu/Cr ternary catalysts during methanol synthesis conditions provided the most detailed information on surface species. At steady state the 80/10/10 Zn/Cu/Cr catalyst had mainly methoxy groups, some formate groups, and no observable formaldehyde groups on the surface (Fig. 6). The adsorbed carbonyl had shifted from 2089 to 2021 cm<sup>-1</sup>, indicating a weakening of the carbon-oxygen bond without changing the nature of the carbonyl (linear bonded). Unfortunately, the hydroxyl region was too distinct to detect any band at 3520 cm<sup>-1</sup>.

The steady-state spectrum of surface species on a binary catalyst during methanol synthesis using a feed with formic acid was very similar to the spectra for feed mixtures of CO/H<sub>2</sub> or CO/CO<sub>2</sub>/H<sub>2</sub> (Fig. 4). Because the spectrum from the formic acid experiment showed no carbonyl species or gaseous carbon monoxide, the evidence for a reaction sequence involving formate and methoxy intermediates was strengthened. A reaction pathway involving carbon-bonded intermediates is unlikely since the lack of formate decomposition provides no carbon monoxide for this synthesis route. Alternatively, a ternary catalyst was unsatisfactory for methanol synthesis using a feed with formic acid. The infrared spectra showed very little formate and methoxy groups on this catalyst, apparently because formic acid decomposition was difficult at these conditions.

The various zinc sites proposed to be involved in this mechanism can be associated with specific crystal planes of zinc oxide (14). The isolated hydroxyls (bands at 3665 and 3620 cm<sup>-1</sup>) are on the same sites as formaldehyde and methoxy species. These isolated hydroxyl sites (Zn<sub>4</sub>) have been associated with polar ZnO surfaces (15). The formate groups occupy a portion of the hydrogen-bonded hydroxyl sites (Zn<sub>g</sub>) which have been associated with nonpolar ZnO surfaces. The hydrogen-bonded hydroxyls have bands at 3550 and 3450 cm<sup>-1</sup>. The site of hydrogen adsorption (Zn<sub>g</sub>), which produces a hydroxyl band at 3520 cm<sup>-1</sup>, is proposed to be a stepped surface between polar and nonpolar planes of zinc oxide.

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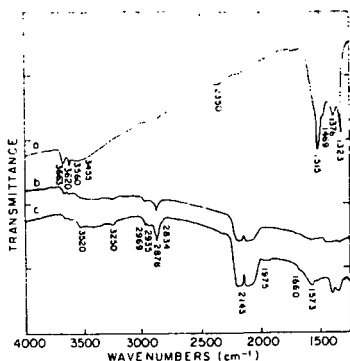


FIG. 1. Carbon monoxide adsorption on 95/5 Zn/Cu oxide at 50 atm and 200°C. (a) Oxidized surface (without pretreatment). (b) exposure for 8 h, and (c) exposure for 24 h.

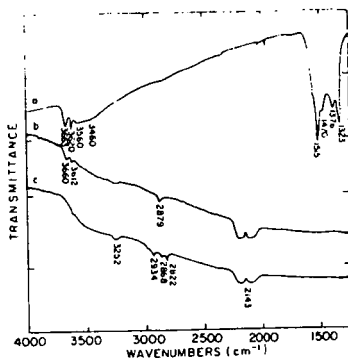


FIG. 2. Adsorption of CO-H<sub>2</sub> mixture on 95/5 Zn/Cu oxide at 50 atm and 200°C. (a) Oxidized surface, (b) exposure for 15 min, and (c) exposure for 1 h.

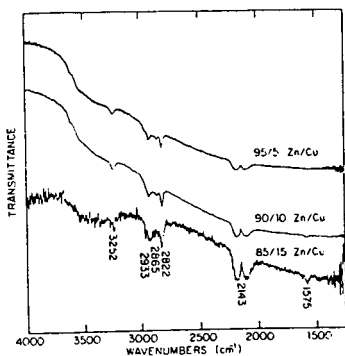


FIG. 3. Adsorption of CO-H<sub>2</sub> mixtures on binary oxides at 50 atm and 200°C.

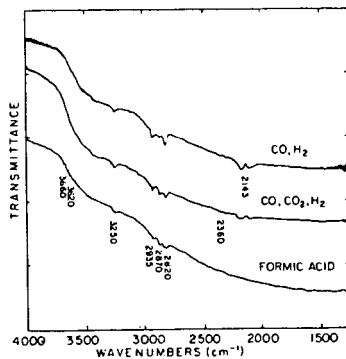


FIG. 4. Adsorption of various feed mixtures on 95/5 Zn/Cu oxide at 50 atm.

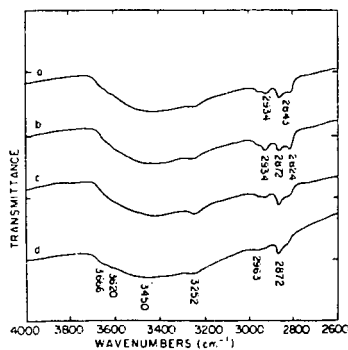
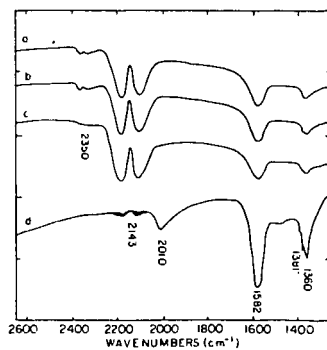


FIG. 5. Adsorption of CO-H<sub>2</sub> mixture on 90/5/5 Zn/Cu/Cr oxide at 50 atm and 200°C. (a) Exposure for 15 min, (b) exposure for 30 min, (c) exposure for 8 h, and (d) after pressure drop.



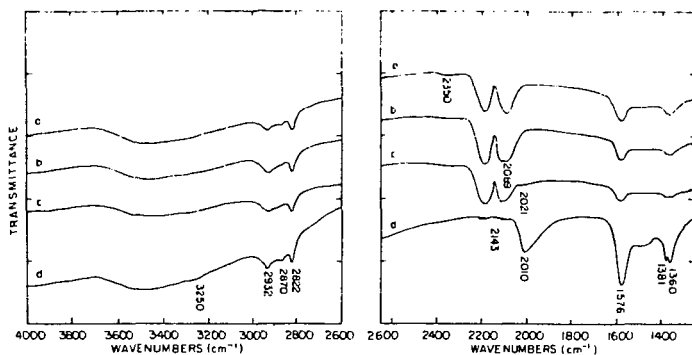


FIG. 6. Adsorption of CO-H<sub>2</sub> mixture on 80/10/10 Zn/Cu/Cr oxide at 50 atm and 200°C. (a) Exposure for 15 min. (b) exposure for 1 h. (c) exposure for 4 h. and (d) after pressure drop.

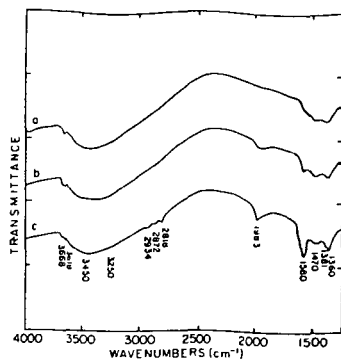


FIG. 7. Adsorption of formic acid on 80/10/10 Zn/Cu/Cr oxide at 50 atm and 200°C. (a) Reduced surface. (b) exposure for 1 h. and (c) exposure for 3 h.